

Analysis of an archive sample from the carbonatic manganese ore sequence, Eplény, Hungary

Egy archív minta vizsgálata az eplényi mangánkarbonátos ércből

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(5 ábra, 2 táblázat)

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Abstract

A typical Jurassic Mn-carbonate ore sample from Eplény consists of manganoan calcite and calcian rhodochrosite, with a moderate amount of quartz. The Mn content of the ore is only 7.51 wt. % (Mn) and the Mn/Fe ratio is 8.73. The Eplény ore differs from the Úrkút Mn-carbonate ore in mineralogical, chemical, and isotopic characteristics. The C isotope data for the Eplény ore ($\delta^{13}\text{C}_{\text{PDB}}: -2.20\text{‰}$) shows that the carbon was derived predominantly from seawater bicarbonate, possibly by direct precipitation. On the other hand, the Úrkút Mn-carbonate mineralization shows more negative isotopic values, indicating a bacterially mediated diagenetic source for the carbon in addition to seawater bicarbonate.

Összefoglalás

Egy tipikus, az Eplényi Mangánérc Bányából származó mangán-karbonát ércminta a röntgen-pordiffrakciós vizsgálatok alapján Mn-tartalmú kalcitból, Ca-tartalmú rodokrozitból és közepes mennyiségű kvarcból áll. Az érc Mn-tartalma 7,51 s%, a Mn/Fe arány 8,73. A vizsgált eplényi karbonátos Mn-érc ásványtani, kémiai és stabil szénizotópos összetétele eltér az úrkútiétól. Az eplényi érc C izotóp összetétele ($\delta^{13}\text{C}_{\text{PDB}}: -2.20\text{‰}$) azt mutatja, hogy a C uralkodóan a tengervíz bikarbonát tartalmából valószínűleg közvetlen kicsapódással ered, míg az úrkúti Mn-karbonátos ércesedés negatívabb C izotóp értékei a tengeri bikarbonát mellett a bakteriálisan befolyásolt diagenetikus szénforrás jelenlétére utalnak (szervesanyag).

Introduction

Among the Hungarian Jurassic Mn-ore deposits, the Úrkút and Eplény deposits are worthy of mention because of their economic significance (Fig. 1). These two manganese occurrences are separated by about 40 km in the Bakony Mountains in the Transdanubian Range. Both deposits are bounded by NW–SE fault systems. The Úrkút deposit is much larger, covering approximately 10 km², and has been exploited since 1917 to the present. The amount of recovered Mn-oxide ore (up to 1997) is 6.3×10^9 kg and Mn-carbonate ore is 1.538×10^9 kg. Many papers and books have been published on the geological, stratigraphical, mineralogical, depositional, and geochemical characteristics of the black shale-

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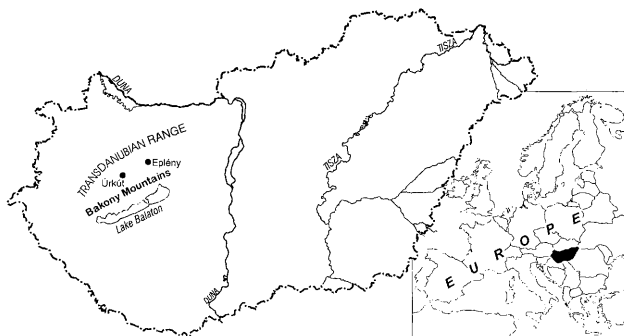


Fig. 1 Geographical location of Eplény and Úrkút

1. ábra. Eplény és Úrkút földrajzi elhelyezkedése

hosted Mn-carbonate and secondarily Mn-oxide ore (e.g., SZABÓ-DRUBINA 1959; GRASSELLY & CSEH NÉMETH 1961; CSEH NÉMETH et al. 1980; SZABÓ & GRASSELLY 1980; GRASSELLY et al. 1981; GALÁ CZ 1984; GRASSELLY & PANTÓ 1988; VARENTSOV et al. 1988; POLGÁRI et al. 1991, 1992; POLGÁRI 1993; POLGÁRI et al. 2000).

The Eplény Mn-ore deposit is smaller than the Úrkút deposit, but very similar to the so-called Csárdahegy-type Mn ore at Úrkút (for description see CSEH NÉMETH 1967). The Eplény deposit covers only about 1 km². The Eplény Mn-oxide ore was exploited both in open pits and underground mines between 1935 and 1975, when the mine was closed. The amount of recovered ore was 766 kt of Mn-oxide ore. When mining was in operation, analytical investigations concentrated on the economically important Mn-oxide ore, whereas the Mn-carbonate ore, which is important from a genetic standpoint, was given very little attention. Once the mine was closed, there was no opportunity to collect new samples for modern investigations and that is why it is important to publish new data on archive samples.

The aim of this paper is to provide new mineralogical, chemical, trace element, and C- and O- isotope data on a typical Mn-carbonate ore sample from the Jurassic, Eplény Mn-carbonate ore. The sample belongs to a collection which was gathered in the 1960s by Professor Gyula GRASSELLY, and was kindly offered for further study by the Petrological and Geochemical Department of Szeged University. We also provide a brief comparison of the characteristics of the Úrkút and Eplény Mn-carbonate ores. It must be emphasized that the importance of preserving samples for future study is fundamentally important. The changing methods of investigation and lack of access to closed mines make archive samples of particular value.

Geological setting

The Eplény Mn-ore deposit occurs in a fault-bounded area that typifies the structure of the Bakony Mountains and has strongly fractured zones and vertical and horizontal fault offsets. The deposit is bounded on the NE by a recurrently reactivated fault zone. The Jurassic sequence at Eplény is not continuous and overlies the Triassic pale whitish-grey microcrystalline Dachstein Limestone. The Dachstein Limestone is overlaid by a Lower Liassic Kardosrét Limestone that is often oolitic and contains foraminifers and brachiopods. The upper part of the Lower Liassic belongs to the "red Jurassic", which includes reddish and pinkish brachiopod-bearing and crinoidal, sometimes cherty limestone ("Hierlatz", Tűzkövesárók and Isztimér Limestone Formations). The Middle Liassic consists of red nodular or massive crinoidal limestone and red-green spotted cherty limestone (Kisgercesse Marl Formation). The Mn deposits rest locally on different types and stratigraphic levels of basement rock. Small Mn-oxide grains and, at some places, lenticular Mn-oxide occur in the crinoidal limestone near the ore bed. The manganese was deposited on an irregular, partly dissolved discontinuity surface of the Lower Jurassic limestone. The relief of the irregular surface of the limestone basement can reach 20–40 m, but averages about 2–5 m. The contact between the underlying limestone and the Mn-ore is sharp, and a transitional zone cannot be seen, except locally on a centimetre scale. Mn-oxide coatings on grain and fracture surfaces are common. A highly characteristic feature is where the Mn-oxide fills the dissolved parts, cavities and vugs, of the Hierlatz-type limestone. Sedimentary dikes composed of Lower and/or Middle Liassic micrite are very characteristic in the NE part of the district.

The average thickness of the Mn deposit is 6–8 m. The main features of the deposit were described in detail (SZABÓ-DRUBINA 1959; GRASSELLY *et al.* 1969; CSEH NÉMETH *et al.* 1980; GRASSELLY *et al.* 1985, 1990), and a summary of those results was provided by POLGÁRI *et al.* (2000). The sketch geological map of the ore deposit is shown in Fig. 2. The Mn-ore section consists of the following parts from the top to bottom:

- Radiolarian claymarlstone (black shale) with lenticular, bedded, finely laminated, blocky Mn-carbonate-bearing claymarlstone.
- Upper part of the ore: dark-grey, black, pyritiferous claystone, claymarlstone with hard, nodular, lenticular, blocky, or poorly consolidated Mn-oxide ore.
- Lower part of ore: primary Mn-oxide ore in yellow, brown, black, phosphorous-rich claystone.

The ore is offset by the Géza fault (Fig. 2). It separates the hard, nodular Mn-oxide ore from the mainly poorly consolidated, layered, bedded-lenticular ore type. The black, dark-grey, finely laminated pyritiferous, radiolarian claymarlstone contains the primary Mn-carbonate lenses, which can be found over a much larger area than the Mn-oxide ore. The Mn-carbonate lenses are accompanied in places by yellow, brown, or red claystone, with the dominant clay mineral being smectite. Mn-carbonate and phosphorite layers and nodules also occur within the Mn-oxide horizon. The heteropic facies of the Mn-carbonate ore is black or varicoloured claystone. Commonly, Ca-carbonate grades

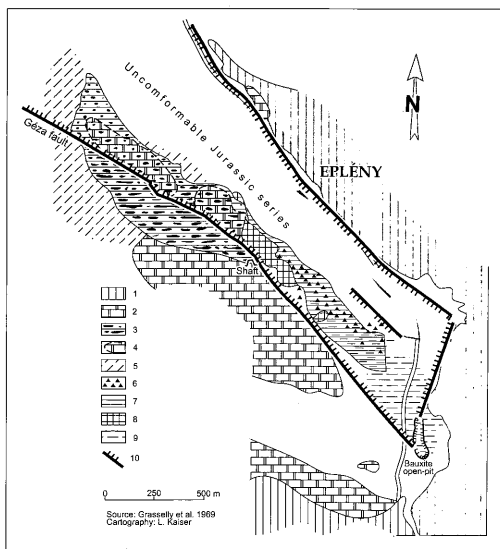


Fig. 2 Geological sketch map of the Eplény manganese deposit (after Grasselly et al., 1969). Legend: 1 Triassic rocks on the surface; 2 Jurassic rocks on the surface (Lower–Middle Liassic); 3 "Primary" Mn-oxide ore (Upper Liassic) differences in legend reflect differences in the intensity of Mn oxide mineralization; 4 "Primary" claymarlstone with Mn-carbonate (Upper Liassic); 5 Limestone facies (Upper Liassic); 6 Reworked Mn-oxide ore (Lower Cretaceous – Middle Eocene); 7 Grey claystone with Mn-carbonate (Lower–Middle Eocene); 8 Oxidized variety of the grey claystone No. 7 (Lower – Middle Eocene); 9 Bauxitic clay (Lower – Middle Eocene); 10 Fault

2. ábra. Az eplényi mangántelep vázlatos földtani térképe (GRASSELLY et al., 1969 alapján). Jelkulcs: 1. triász kőzetek a felszínen; 2. jura kőzetek a felszínen (alsó–középső-liász); 3. „primér” oxidos Mn-érc (felső-liász) (a jelkulcs különbség a Mn-oxid ércesedés intenzitásának különbségét tükrözi); 4. „primér” agyagmárga Mn-karbonáttal (felső-liász); 5. mészkő (felső-liász); 6. újrafeldolgozott oxidos Mn-érc (alsó–kréta–középső-eocén); 7. szürke agyag Mn-karbonáttal (alsó–középső-eocén); 8. oxidált szürke agyag (7) (alsó–középső-eocén); 9. bauxitos agyag (alsó–középső-eocén); 10. törésvonal

laterally into pale Mn-carbonate layers in the black manganiferous claystone. The hanging-wall rock is claystone, similar to the heteropic facies described above.

Previous studies

In the 1950s a limited number of descriptions of Mn-carbonate-ore samples – including light microscopy observations, examination of the major element contents, and mineralogical investigations were done by one of the present authors (M. SZABÓ-DRUBINA). Part of these results were published at that time (SZABÓ-DRUBINA 1959), but important data (e.g. micromineralogical) remained

unpublished. In the paragraph below we give a summary of both the published and unpublished results.

The Mn-carbonate layers are soft or hard, depending on the amount of rhodochrosite or other carbonate minerals present (SZABÓ-DRUBINA 1959). The ore is very fine-grained, with a porosity of 15–20%. The carbonate mineral content is 35–50 wt.%. The Mn content is 15–18 wt.% and the SiO_2 content is 20–28 wt.%. Calcite and rhodochrosite contents generally show a negative correlation. The P_2O_5 content is higher than 1 wt.%, and the S content is 0.8–4.0 wt.%, which reflects the presence of pyrite. Rhodochrosite- and calcite-rich laminae alternate with smectite- and pyrite-rich laminae. Lesser amounts of detrital quartz, as well as limonite and glaucony also occur. (We note that the green, rounded mineral, – called “glauconite” in the original paper – was not analysed by any chemical or structural methods. It could be either chlorite or mica, thus here consider it only as “glaucony”. This mineral phase differs, even at first appearance, from the typical colour-giving, fine-grained green mica, (celadonite), of the Úrkút manganese carbonate ore (WEISZBURG *et al.* 2003).

The above description was based on the study of a limited number of samples from which the location of 8 samples (collected from three points of two dip slope shafts, see symbol #22 on Fig. 3) can be reconstructed. These samples are laminated claystones (yellow, red, greenish, greyish, black, or brown) with Mn-carbonate layers. Locally, pyrite nodules occur with diameters of 0.2–1.5 cm. Smectite and limonite were determined by DTA.

Under a polarized light optical microscope the clay- and carbonate-rich parts occur in distinct laminae. Opaque (pyrite) and green grains (glaucony?) and scarce quartz grains can also be found. Some of the samples are rich in microfossils (foraminifers, ostracods, sponge spicules, crinoid fragments etc.).

The heavy mineral part of the > 0.1 mm fraction (200 grains) contains 80% pyrite, a 8.5% limonite weathering crust (grain coating fragments), 7% brown-altered grains (glaucony-like), 3% glaucony(?), 1% brown amphibole, and 0.5% dolomite. The 0.06–0.1 mm size range (200 grains) was represented by 64% pyrite, 24% brown-altered grains (glaucony-like), 5% brown amphibole, 3% glaucony(?), 2.5% dolomite, 0.5% chlorite, titanite, and actinolite.

The light fraction (300 grains, in both fractions) contains 99% brown-altered grains (glaucony-like), and 1% quartz and glaucony(?).

Sample, methods and results

One massive Mn-carbonate sample (Ref. # GR31) was found during a review of the collection of Professor Gyula GRASSELLY (Szeged) in 2001. The sample was collected in the 1960s from the underground mine +260 m level and had not been studied previously. The sample is white to pale grey, porous, homogeneous, with subtle layering. The sample location is shown on Fig. 4. The outer surface weathers dark-brown-grey because of oxidation of the Mn(II).

That Mn-carbonate ore sample from the Eplény Mine was first analysed using a polarized light optical microscope.

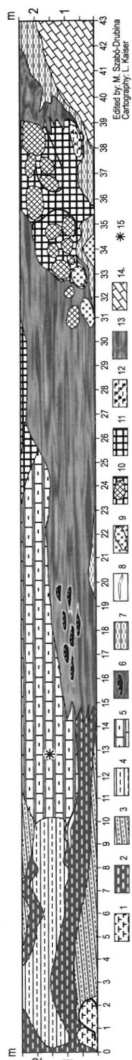


Fig. 4 Geological profile of the Mn-carbonate ore lens with the location of the sample investigated here (+260 m level, 120–300°). The location of the studied profile is shown in Fig. 3. Legend: 1 Chert nodules with Mn-oxide vein fillings and calcite; 2 Bedded, black claymaniferous claystone; 3 Black manganese claystone; 4 Bedded clayey Mn ore; 5 Mn-carbonate ore; 6 Black clay (white lenses at the upper part); 7 Yellow clay with white chert layers; 8 White Mn-carbonate lens below the Mn-oxide nodule; 9 Nodular crystalline Mn-oxide ore; 10 Blocky Mn-oxide ore; 11 Mn-oxide ore; 12 Black Mn-bearing clay with red spots; 13 Black claystone; 14 Limestone (footwall); 15 Sample studied

4. ábra. Mn-karbonátos érlelence földtani szelvénye a vizsgált minta gyűjtési helyével (+260 m szint, 120–300°). A vizsgált szelvény helyzete a 2b ábrán látható. Jelekulcs: 1. tűzkőgumók Mn-oxidál és kalcittal; 2. réteges, fekete agyag; 3. fekete, mangános agyag; 4. réteges, agyagos Mn-érc; 5. karbonátos Mn-érc; 6. fekete agyag, a felső részén fehér lencsék; 7. sárga agyag fehér tűzkő rétegekkel; 8. fehér Mn-karbonát lencse Mn-oxidos ércgumó alatt; 9. gumós, kristályos, oxidos Mn-érc; 10. darabos oxidos Mn-érc; 11. oxidos Mn-érc; 12. vörösfoltos, fekete Mn-os agyag; 13. mészkő (fekü); 14. mészkő (fekü); 15. a vizsgált minta gyűjtési helye

using a step size of $0.02^\circ 2\theta$ at 1 s/step, yielding a scan speed of $0.02^\circ 2\theta/s$. Semi-quantitative estimates of relative mineral percentages were obtained from peak intensities, which were multiplied by the weighting factors used by the Ocean Drilling Program (COOK et al. 1975), and normalized to 100%. Mineral contents are listed as major (>25%), moderate (5–25%), and minor-trace (<5%). Carbonate element substitutions (i.e. calcian rhodochrosite) were determined by deviations of the position of the 100% intensity carbonate reflection, as determined using an internal quartz standard, from stoichiometric carbonate end members.

Major and trace element analysis was done by XRAL Laboratories, Canada. The details of the methods applied are described in POLGÁRI et al. (2002).

Stable C- and O-isotope composition was determined by the routine methods of the USGS.

The sample consists of microcrystalline carbonates and rare opaque grains (probably pyrite). Microfossils were not found in the thin section. The X-ray diffraction mineralogy (normalized to 100%) shows about 65 wt.% manganoean calcite, 20 wt.% quartz, and 15 wt.% calcian rhodochrosite (Table 1). The Mn content of the ore is relatively low at 7.51%, and the Mn/Fe ratio is 8.73 (Table 2). The CaO content is high and reflects predominantly the manganoean calcite contents, as is the SiO_2 , which reflects the content of

Table 1 Results of X-ray diffraction analysis on the Eplény and Úrkút Mn-carbonate-ore types
1. táblázat. Az eplényi és úrkúti karbonátos Mn-érc típusok ásványos összetétele (XRD)

		Ore type	Mineral composition		
			Major	Moderate	Trace
EPLÉNY *		Carbonate ore	Manganoan calcite ($d_{(104)} : 2.97\text{Å} - 3.04$)	Calcian rhodochrosite ($d_{(104)} : 2.85 - 2.88\text{Å}$) Quartz	-
ÚRKÚT* *		Bed No II. (4 samples)	Siderite, rhodochrosite	Calcite, pyrite	10Å phyllosilicate
Main ore bed***	top	Grey-type (10 samples)	Rhodochrosite, pyrite	Calcite, smectite, 10 Å phyllosilicate, glauconite-celadonite	Zeolite, chlorite
		Brown-type (10 samples)	Rhodochrosite, 10 Å phyllosilicate (glauconite- celadonite)	Goethite	Smectite, pyrite, calcite, quartz, anatase, rhodochrosite
	bottom	Green-type (8 samples)	Rhodochrosite, 10 Å phyllosilicate (glauconite- celadonite)	Goethite	Quartz, haematite, rutile

*Current study

**For the profiles and sample descriptions and detailed data see POLGÁRI et al. (1991)

***This is the general division, but alternating green, brown and grey layers can occur anywhere

quartz. Minor clay minerals probably occur as indicated by the low amounts of Al, K, and Mg. The trace element and rare earth element contents of the sample are relatively low.

There is a very good agreement between the mineral phase compositions calculated from the chemical analysis and derived directly from the X-ray diffractometry.

The $\delta^{13}\text{C}_{\text{PDB}}$ is -2.20‰ , the $\delta^{18}\text{O}_{\text{PDB}}$ is -0.25‰ (Fig. 5).

Comparison of the Eplény and Úrkút Mn-carbonate ores

The Eplény Mn-carbonate ore differs from the Úrkút main (No I.) and bed No II. ores because its main ore mineral is manganoan calcite, with calcian rhodochrosite being much less abundant; this is in contrast to rhodochrosite being dominant at Úrkút, with lesser amounts of siderite. In addition, unlike the Úrkút deposit, the Eplény ore has moderate amounts of quartz, but only minor clay minerals. According to major elements data (Table 2), the Si content of the Eplény ore is similar to the main (No I.) bed and bed No II of the Úrkút deposit, but the Al, K, and Mg concentrations are much less than in the Úrkút ores because of the near absence of clay minerals at Eplény. The total Fe content is also very low in the Eplény ore compared to Úrkút, where Fe is hosted by green clay minerals, goethite, siderite, and pyrite; apart from pyrite, there are all absent in the massive Eplény ore. P, Ti, Ba, and Sr concentrations and the trace and rare earth elements are also not enriched in the Eplény ore. The Ca concentration is approximately four times higher in the Eplény ore than at Úrkút.

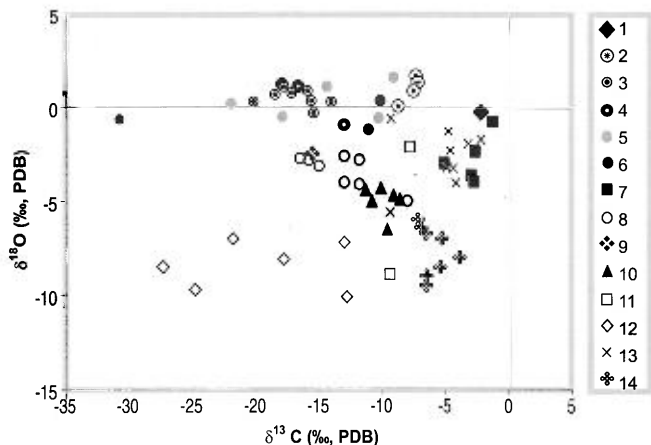


Fig. 5 Relationships between $\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{PDB}}$ values of Mn-carbonate ores from Eplény (current study), Úrkút (POLGÁRI et al. 1991), Molango (Mexico, OKITA et al. 1988), Moanda (Gabon, HEIN et al. 1989) and Wafangzi, Minle, Datangpo, Gaoyan, and Taojiang (China, FAN et al. 1996). Legend: 1 Eplény, Mn-carbonate ore; 2 Úrkút, green-grey Mn-carbonate ore; 3 Úrkút, brown, black Mn-carbonate ore; 4 Úrkút, green Mn-carbonate ore; 5 Úrkút, grey Mn-carbonate ore from bed No. II; 6 Úrkút, black shale; 7 Molango; 8 Molango; 9 Moanda; 10 Minle; 11 Datangpo; 12 Taojiang; 13 Gaoyan; 14 Wafangzi

5. ábra. Karbonátos Mn-ércék $\delta^{13}\text{C}_{\text{PDB}}$ és $\delta^{18}\text{O}_{\text{PDB}}$ értékeinek kapcsolata (Eplény, jelen tanulmány, Úrkút (POLGÁRI et al. 1991), Molango (Mexikó, OKITA et al. 1988), Moanda (Gabon, HEIN et al. 1989) és Wafangzi, Minle, Datangpo, Gaoyan, és Taojiang (Kína, FAN et al. 1996). 1. Eplény, karbonátos Mn-érc; 2. Úrkút, zöld-szürke, karbonátos Mn-érc; 3. Úrkút, barna-fekete, karbonátos Mn-érc; 4. Úrkút, zöld, karbonátos Mn-érc; 5. Úrkút, szürke, karbonátos Mn-érc; 6. Úrkút, szürke, karbonátos Mn-érc a II. telepéből; 7. Úrkút, feketepala; 8. Molango; 9. Moanda; 10. Minle; 11. Datangpo; 12. Taojiang; 13. Gaoyan; 14. Wafangzi

The C isotopic composition (-2.20‰) of the current Eplény Mn-enriched carbonate "ore" sample (Mn 7.51 wt.%) differs from that of the typical, rich Úrkút Mn ore (Mn 17–37 wt.%; $\delta^{13}\text{C}$: $-8 - -30\text{‰}$, mean: -14.6‰), but is similar with respect to the low (< 7 wt.%) Mn-containing Úrkút carbonate samples ($\delta^{13}\text{C}$: $0 - -5\text{‰}$) (POLGÁRI, 1993). The $\delta^{18}\text{O}_{\text{PDB}}$ is similar to the Úrkút ore values (Fig. 5).

Discussion of the stable isotope data and the genetical model of the deposit

Many papers have been published on the connection between the origin of Mn-carbonate deposits and the $\delta^{13}\text{C}$ isotope values (FROELICH et al. 1979; IRWIN et al. 1977; OKITA et al. 1988; HEIN et al. 1989; POLGÁRI et al. 1991). Based on that background the low negative $\delta^{13}\text{C}$ value of the manganese-enriched carbonatic

Mo	-	-	5	bdl (<2)	-	-	-	-	-	-	-	-	-	-
Ni	-	-	82	15	16	14	213	25	-	23	57	84	46	48
Pb	-	-	88	13	29	33	35	33	-	31	128	83	151	396
Ti	-	-	1450	-	-	-	-	-	-	-	-	-	-	-
V	-	-	129	19	-	-	-	-	-	-	-	-	-	-
Zn	-	-	560	17	48	40	64	74	-	56	35	35	32	28
Se	-	-	-	4.0	2.2	3.9	5.2	3.7	-	4.4	4.2	2.9	3.2	4.7
As	-	-	-	bdl (<10)	40	127	14	24	-	13	25	23	31	28
Hf	-	-	-	-	0.5	0.5	0.5	0.5	-	1.4	1.2	0.8	0.9	1.1
Th	-	-	-	7.00	1.0	1.0	2.5	2.5	-	3.9	3.2	1.8	2.2	3.4
U	-	-	-	bdl (<100)	1.8	1.0	3.7	1	-	1.3	0.8	0.6	1.5	1.4
Rb	-	-	-	-	100	100	100	-	-	80	30	56	43	32
Y	-	-	-	31	-	-	-	-	-	-	-	-	-	-
Nb	-	-	-	5.0	-	-	-	-	-	-	-	-	-	-
La	-	-	-	30	32	62	74	44	33	55	47	43	43	44
Ce	-	-	-	153	89	200	195	188	92.2	165	161	136	129	124
Nd	-	-	-	31	30	50	50	30	21.0	51.8	33.8	29.6	34.5	32.6
Sm	-	-	-	-	6.7	14	13.2	16.8	9.4	13.1	11.5	10.5	9.8	12.7
Eu	-	-	-	bdl (<2)	1.06	2.47	2.4	1.97	0.99	1.66	1.59	1.46	1.42	1.68
Tb	-	-	-	-	1.0	2.0	1.2	0.9	2.3	1.7	1.2	1.2	1.1	1.5
Tm	-	-	-	-	2.0	2.0	2.0	0.5	1.1	1.1	0.8	0.8	1.1	0.8
Yb	-	-	-	2.0	1.9	3.5	5.1	2.5	2.6	2.9	2.9	2.6	2.5	3.0
Lu	-	-	-	-	0.15	0.53	0.65	0.32	0.39	0.49	0.41	0.38	0.34	0.45
Ho	-	-	-	bdl (<4)	-	-	-	-	-	-	-	-	-	-
Ta	-	-	-	bdl (<40)	-	-	-	-	-	-	-	-	-	-

*the number of samples from which the means were calculated are in parentheses; bdl: below detection limit

**calculation of CO₂ from (Mn+Ca)CO₃

1. grey, dark-grey layered Mn-carbonate ore, Eplény, analyst: Ms. GUCZY K., Hungarian Geol. Inst. (in SZABÓ-DRUBINA (1959), page 130, sample code 4; sample location is in Fig. 3,
2. average value from unknown samples, Eplény Mine (in: POLGÁRI et al. (2000), page 344.)
3. OES average data of Mn-carbonate samples from Eplény Mine (sample location is in Fig. 3): analyst ZENTAY P. 1966–67, Hungarian Geol. Inst.; from POLGÁRI et al. (2000), page 348
4. Current study, Eplény; analysed by XRAL Laboratories, Canada, 2002
5. Kövestábla, Űrkút, grey Mn-carbonate ore from POLGÁRI et al. (2000), page 117 and 205, sample code 148
6. Kövestábla, Űrkút, green Mn-carbonate ore from POLGÁRI et al. (2000), page 117 and 205, sample code 150
7. Lejtőszakna, SE field, Űrkút, grey Mn-carbonate ore from POLGÁRI et al. (2000), page 117 and 205, sample code 139
8. Kislőd mine, Űrkút, brown Mn-carbonate ore from POLGÁRI et al. (2000), page 118 and 205, sample code 156
9. Csárdahegy, Űrkút, green-grey Mn-carbonate ore, bed No. II from POLGÁRI et al. (2000), page 120 and 205, sample code 179
10. Űrkút mine, shaft No. III and Nyíres field, green-grey, Mn-carbonate ore from POLGÁRI et al. (2000), page 197–198
11. Űrkút mine, shaft No. III and Nyíres field, brown, black Mn-carbonate ore from POLGÁRI et al. (2000), page 197–198
12. Űrkút mine, shaft No. III and Nyíres field, green Mn-carbonate ore from POLGÁRI et al. (2000), page 197–198
13. Űrkút mine, shaft No. III and Nyíres field, grey Mn-carbonate ore from POLGÁRI et al. (2000), page 197–198
14. Űrkút mine, shaft No. III and Nyíres field, grey Mn-carbonate ore bed No. II from POLGÁRI et al. (2000), page 197–198
- 10–14 (total S, S²⁻, and organic C from profile A, shaft No. III, Űrkút mine; see POLGÁRI (1993)

“ore” from Eplény can be connected to three different genetical processes or a combination of these processes.

Black shale environment, bacterial contribution with changing Mn content, or with changing bacterial Mn-reducing activity

A number of papers have already established a genetic model of Mn-carbonate deposits in which Mn-oxide is first precipitated at the seafloor and then during early diagenesis; under reducing conditions Mn^{4+} is reduced to Mn^{2+} , coupled with the bacterial oxidation of organic matter. This produces CO_2 to form MnCO_3 (e.g. OKITA et al. 1988). The $\delta^{13}\text{C}_{\text{PDB}}$ of carbonates formed solely from CO_2 derived from the oxidation of organic matter would have values of about -22 to -32‰ , depending on the isotopic composition of the organic matter. If the carbonate is formed from seawater bicarbonate ($\delta^{13}\text{C}_{\text{PDB}}$ of about 0‰) as well as from CO_2 produced by the oxidation of organic matter, then it can have an isotopic composition between those end members. Mn-carbonate ore deposits hosted by black shales, such as the giant Moanda (Gabon), Taojiang (China), and Úrkút (Hungary) deposits belong to this type of bacterially mediated, mixed carbon source-type deposit (Fig. 5).

One of the factors controlling the carbon source of the carbonates of a given sediment sequence can be just the total manganese available for bacterial mediation: a low amount of manganese limits the bacterial contribution, so that carbonates (e.g. calcite) precipitated directly from the seawater become dominant in the samples.

The similarity of the isotope data of the lower Mn content sample of the Eplény ore to that of the low Mn content samples from Úrkút ores may support that genetical model.

Another factor producing a similar result could be the type of the bacterial activity itself. In the sulfate-reduction zone microbially formed HS^- forms FeS which can reduce Mn-oxide; rhodochrosite can be precipitated from the reduced Mn, and HCO_3^- from seawater; at the same time, S^{2-} oxidizes to SO_4^{2-} , which further supports the activity of sulfate-reducing bacteria.

Black shale environment with a changing oxygen content (anoxic-oxic development) without bacterial contribution

During the last few years some authors have published results on black shale-hosted Mn-carbonate deposits that show $\delta^{13}\text{C}_{\text{PDB}}$ values of around 0‰ . FAN et al. (1996) compared seven Chinese deposits and concluded that the Gaoyan-type Mn-carbonate were formed by primary sedimentary processes. They suggested that the depositional environment changed from anoxic (black shale) to slightly oxidized (represented by Mn-carbonate ore).

KRAJEVSKY et al. (2001) published $\delta^{13}\text{C}_{\text{PDB}}$ data of -1.2 to $+0.5\text{‰}$ for the Banie Mn-Ore Bed, Lower Jurassic Huciska Limestone (Lower Sub-Tatric Nappe in the Western Tatra Mountains, Slovakia).

These authors propose that there was only a minor biotic influence when the ores themselves were precipitated directly from seawater. In an anoxic environment, manganese is soluble as Mn^{2+} and is stored in solution in the basin waters. When the environment changes to slightly oxidized and alkaline, a large amount of the manganese can be precipitated directly to form manganese carbonate (micritic or micro-spheroidal). This primary Mn-carbonate may be further enriched with to its Mn content during early diagenesis (FAN *et al.* 1996).

In such a case the measured C-isotope value would indicate that the carbon was derived from seawater bicarbonate, possibly by direct precipitation; this is typical for Mn-carbonate ores of low-temperature origin (HUDSON 1977).

A purely biogenic origin

The study of the black shale-hosted Mn mineralizations shows that microbes may be involved in the ore-forming processes in several ways. The catalytic effect of microbes is important in the cycling of manganese.

Another very complex microbial system exists that can influence an Mn-carbonate formation which contains relatively heavy C via the following processes:

- In oxygen-deficient marine basins, the manganese from different sources accumulates in a dissolved form and bacteria and algae may adsorb and adhere metal ions, which can also provide Mn to the basin. The interaction between the inorganic system and the biota can be variable; some species of bacteria concentrate manganese and are capable of depositing it. In their cells various algae can also concentrate manganese which has been dissolved in water (KRUMBEIN 1984).

- During sedimentation, the effect of microbes can be direct or indirect. Respiration of microbes produces HCO_3^- and CO_2 , which are assimilated by algae, and the pH of the seawater increases. Under these conditions rhodochrosite can precipitate directly from seawater. Rhodochrosite can be formed through the metabolic processes of microbes (KRUMBEIN 1984).

Conclusions

The Eplény carbonate manganese ore differs from the Úrkút Mn-carbonate ore in several mineralogical, chemical, and isotopic characteristics. The main mineral constituents of the Eplény Mn-carbonate ore sample studied are manganoan calcite and calcian rhodochrosite. The Mn content is low, only 7.51%. The trace element concentrations in the ore are also low. The C isotope data shows that the carbon was derived from seawater bicarbonate, possibly by direct precipitation, whereas the Úrkút Mn-carbonate mineralization shows more negative isotopic values. This indicates a more intense bacterially mediated diagenetic source for the carbon, in addition to seawater bicarbonate. The slightly negative value may be interpreted by the extreme dilution of a bacterially influenced C reservoir (seawater-sourced carbon is about 93%). While the Úrkút Mn-carbonate ore shows a bacterially mediated diagenetic pathway towards its formation, the

sample of Eplény ore indicates direct precipitation from seawater, or a diagenetic system completely open to the influence of seawater. Other scenarios, like the indirect effect of a possible set of microbial processes during the Mn-carbonate formation, need further study.

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